



SYNTHESIS, STRUCTURE AND CHARACTERIZATION OF *p*-CYMENE Ru(II) 2-(BIPHENYLAZO)PHENOLATE COMPLEXES

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Abstract

A series of Ru(II) and Ru(III) complexes of the types $[RuX(CO)(EPh_3)_2L]$ ($X = H, E = P; X = Cl, E = P$ or As) and $[RuX_2(EPh_3)_2L]$ ($X = Cl, E = P$ or $As; X = Br, E = As, L =$ monoanion of dehydroacetic acid) have been synthesized in order to explore their biological activities, such as DNA-binding and antibacterial activity. The complexes were characterized by analytical and spectroscopic techniques. The crystal and molecular structure of $[RuCl_2(AsPh_3)_2(L)]$ has been determined by single crystal XRD. The cyclic voltammograms of the complexes in acetonitrile displayed either quasi-reversible or irreversible redox couples based on the metal centre. The ligand, dehydroacetic acid (DHA) and its metal complexes were tested against five pathogenic bacteria. Absorption titration and cyclic voltammetric studies revealed that the complexes interact with Herring Sperm ds DNA through different binding modes to different extents.

There has been an increasing interest in the chemistry of half sandwich organoruthenium (II) complexes due to numerous applications in new catalytic systems for a variety of organic transformations. Ruthenium(II)-arene complexes display a three-legged piano stool structure in which the metal center has a quasi-octahedral geometry are occupied by an arene ligands. This structural feature opens the possibility to introduce in the molecule by two types of stereogenic centers: the metal and ligands. The O,N-donor type of ligands have been prepared to optimize the catalytic potential of their metal complexes.

Keyword, Dehydroacetic Acid, Ruthenium, Pyrrole-Ketone; Cymene.

Introduction

Many methods for specific catalytic oxidation of various organic substrates such as alcohols, amines, amides and hydrocarbons have been studied extensively using low-valent metal complexes as catalysts. It is to be noted that ruthenium compounds are intensively studied transition metal compounds and many methodologies have been developed with them. Ru-based oxidation catalysis is a powerful and extremely versatile synthetic tool to afford selectively oxygenate products both in homogeneous and in heterogeneous conversions.

Current interest in the chemistry of half-sandwich (η^6 -arene)-ruthenium(II) complexes lies in the development of new catalytic systems for a variety of organic transfer hydrogenations and in the enantioselective asymmetric induction studies. It has been found in the literature that the arylazophenol ligand is known to coordinate metal ions usually in a bidentate fashion with N, O donor forming a five-membered chelate ring. Particularly the azo (-N=N-) group due to its strong π -acid character stabilizes ruthenium in lower oxidation states while phenolate oxygen being a hard base stabilizes the higher oxidation state of the metal ion. The reduction of ketones using catalytic hydrogenation transfer conditions with 2-propanol as hydrogen source has been largely investigated in the last years and several ruthenium complexes have proven to be efficient catalyst precursors in transfer hydrogenation. Mathey and coworkers have reported the cationic Ru-(*p*-cymene)Clchelate complex as catalyst for the hydrogen



transfer process of ketones with very high TON and TOF. Further, ruthenium CN pincer complexes have been reported by Baratta and coworkers as highly active catalysts in the transfer hydrogenation of ketones in 2-propanol with NaOiPr.

The ability of ruthenium complexes to dehydrogenate alcohols and deliver the hydrides to a ketone or an α , β -unsaturated ketone has made them useful as transfer hydrogenation catalysts. The reaction conditions for transfer hydrogenations are economic, relatively mild and environmentally friendly. Metal complexes containing bidentate ligands are normally used as catalysts in transfer hydrogenation reaction and the nitrogen containing ligand lead to an increased catalytic activity.

In particular, half-sandwich ruthenium(II) complexes of the type $[(\eta^6\text{-arene})\text{Ru}(\text{A-B})\text{X}^+\text{X}^-]$ (where A-B is an optically pure chiral bidentate ligand and X is a halide) have found to be efficient catalyst precursors for the transfer hydrogenation of ketones. Recently, bifunctional transition metal-based molecular catalysts for transfer hydrogenation of ketones under different experimental conditions have been reviewed by Ikariya and coworkers. Azophenol complexes of formula $[(\eta^6\text{-p-cymene})\text{RuCl}(\text{L})]$ (L = mono anionic 2-naphthylazo-pmethylphenolate ligand) were used as effective catalyst for reduction of acetophenone. Recently our group has reported ruthenium(III) complexes of amine-bis(phenolate) ligands as catalysts for transfer hydrogenation of a series of aliphatic and aromatic ketones. Further, the influence of arene ring of η^6 -arene ruthenium(II) complexes containing the iminophosphorane-phosphine ligand in catalytic transfer hydrogenation of cyclohexanone have been described.

Three geometrical isomers, (5)-(7), of $[\text{RuL}_2\text{C}_1_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ [L = 2-(phenylazo)pyridine] have been isolated via stereoretentive oxidation of the corresponding ruthenium(II) isomers with concentrated nitric acid. The low-spin ($t_2g^6, S = 0$) complexes display rhombic e.s.r. spectra in frozen solution (77 K). The axial (A) and rhombic (V) distortion parameters (in the order A, V) are (in cm⁻¹): 5 230, -3 520 (5); -5 150, 3 970 (6); and -4 900, 4 610 (7). The sign changes correspond to energy inversion of split t_2g components. The magnitude of V increases with decreasing symmetry as expected, (5) < (6) < (7). Two predicted optical transitions within the Kramers doublets are experimentally observed or indicated in the near-i.r. region [(5), 7 000, < 4 500; (6), 6 900, 5 000; and (7), 6 900, 5 100 cm⁻¹]. The $[\text{RuL}_2\text{Cl}_2]^+[\text{RuL}_2\text{C}_1_2]^-$ couple is reversible in acetonitrile and has $E_{1/2}$ values 0.92, 1.07, and 1.16 V vs. s.c.e. in the cases of (5), (6), and (7) respectively. These potentials correlate linearly with the energy of the highest t_2g component. The complexes bring about the oxidative coupling of N,N-dimethylaniline, the oxidation of tris(1,2-naphthoquinone 1-oximato)nickel(II) to the corresponding nickel(III) complex, and the oxidation of free 1,2-naphthoquinone 1-oxime (Hnqo) to the corresponding iminoxy radical. In the cyclic voltammetric oxidation of $[\text{RuL}_2\text{C}_1_2]$ in the presence of Hnqo the observed current is in excess of the sum of currents due to the components taken separately. This has been analysed in terms of an electrocatalytic model. The excess current as well as the turnover number varies linearly with the ratio of the concentration of Hnqo to that of $[\text{RuL}_2\text{C}_1_2]$ [3].

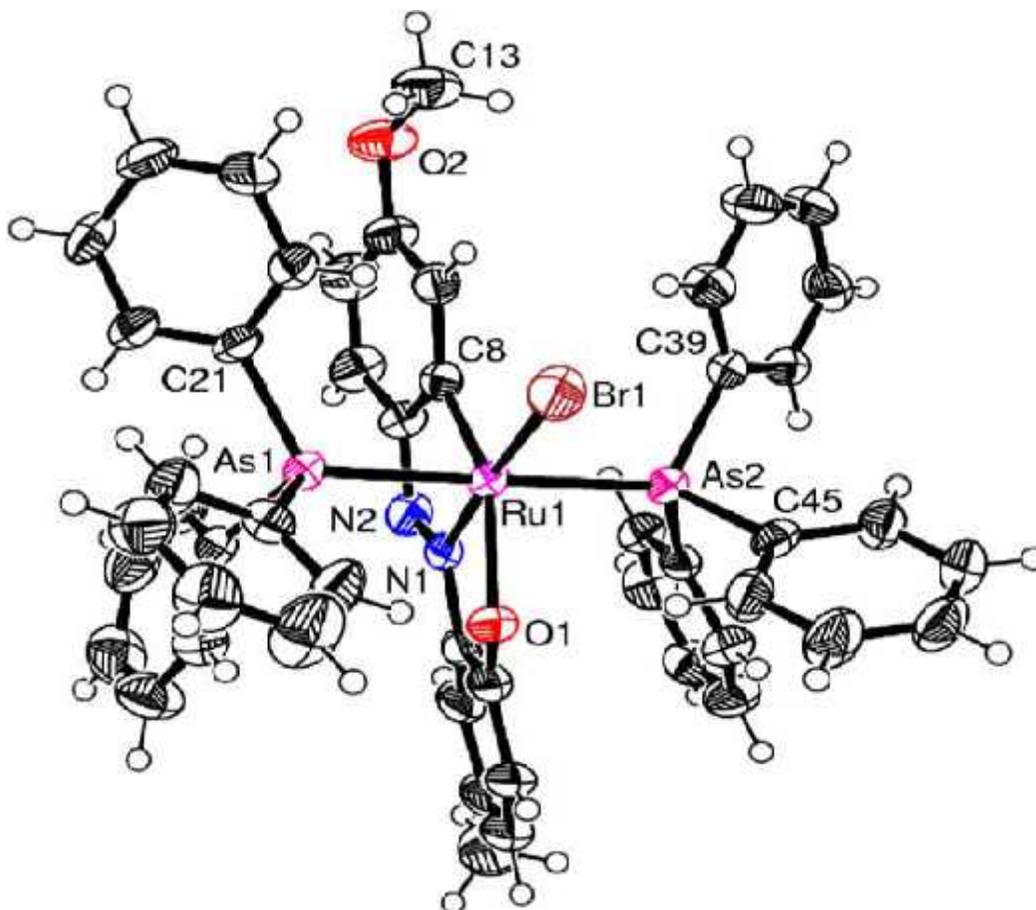
Interaction of 1-(2-pyridylazo)-2-naphthol (PAN) with $[\text{Mo}(\text{CO})_6]$ in air resulted in formation of the tricarbonyloxo-complex $[\text{Mo}(\text{CO})_3(\text{PAN})]$, 1. The dicarbonyl complex $[\text{Ru}(\text{CO})_2(\text{PAN})]$, 3, was obtained from the reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with PAN. In presence of triphenyl phosphine (PPh₃), the reaction of PAN with either $\text{Mo}(\text{CO})_6$ or $\text{Ru}_3(\text{CO})_{12}$ gave $[\text{Mo}(\text{CO})_3(\text{PAN})(\text{PPh}_3)]$, 2, and $[\text{Ru}(\text{CO})_2(\text{PAN})(\text{PPh}_3)]$, 4. All the complexes were characterized by elemental analysis, mass spectrometry, IR, and NMR spectroscopy. The thermal properties of the complexes were also investigated by thermogravimetry [6].



Reaction of 2-(4'-R-phenylazo)-4-methylphenols ($R=OCH_3$, CH_3 , H , Cl , and NO_2) with $[Ru(dmsO)_4Cl_2]$ affords a family of five ruthenium(III) complexes, containing a 2-(aryloxo) phenolate ligand forming a six-membered chelate ring. A similar reaction with 2-(2'-methylphenylazo)-4-methylphenol with $[Ru(dmsO)_4Cl_2]$ has afforded a similar complex, in which 2-(2'-methylphenylazo)-4-methylphenolate ligand is coordinated forming a six-membered chelate ring, and the other two ligands have undergone the C-C coupling ring, a nine-membered N,N-chelate ring, and another five-membered N,O-chelate ring. 2-(2',6'-dimethylphenylazo)-4-methylphenol with $[Ru(dmsO)_4Cl_2]$ has afforded a complex in which two 2-(2',6'-dimethylphenylazo)-4-methylphenols are coordinated as bidentate N,O-donors forming five-membered chelate rings, while the third one has coordinated to the metal center in the iminosemiquinonate form. Structures of four selected complexes have been determined by X-ray crystallography. The first six complex is diamagnetic and shows characteristic 1H NMR signals. All the complexes show intense charge-transfer in the visible region and Ru(III)-Ru(IV) oxidation on the positive side of SCE and a Ru(III)-Ru(II) reduction on the negative side.

Treatment of $[RuCl_3(PPh_3)_3]$ with 1-(aryloxo)naphthol ligands in benzene under reflux afford air-stable new organoruthenium(III) complexes with general composition $[Ru(an-R)Cl(PPh_3)_2]$ (where, $R=H$, Cl , CH_3 , OCH_3 , OC_2H_5) in fairly good yield. The 1-(aryloxo) naphtholate ligands behave as dianionic tridentate C,N,O donors and coordinates to ruthenium through phenolic oxygen, azo nitrogen and ortho carbon generate two five-membered chelate rings. The composition of the complexes have been established by analytical (elemental analysis and magnetic susceptibility measurement) and spectral (FT-IR, UV-Vis, EPR) methods. The complexes are paramagnetic (low-spin, d^5) in nature and in dichloromethane solution show intense d-d transitions and ligand-to-metal charge transfer (LMCT) transitions in the visible region. The solution EPR spectrum of complex $[Ru(an-CH_3)Cl(PPh_3)_2]$ in dichloromethane at 77K shows rhombic distortion around the ruthenium ion with three different 'g' values (g_x , g_y , g_z). The single crystal structure of the complex in these complexes. All the complexes exhibit one quasi-reversible oxidative response in the range 0.60-0.79V $[Ru^{IV}/Ru^{III}]$ and two formal potential of all the couples correlate linearly with the range -0.50 to -0.62 V and -0.93 to -0.98V respectively. The formal potential of all couples correlate linearly with the Hammett constant of the para substituent in aryloxo fragment of the 1-(aryloxo) naphtholate ligand. Figure, the catalytic efficiency of one of the ruthenium complexes was determined for the transfer hydroxylation of ketones with an excellent yield up to 99% in the presence of isopropanol/KOH.

Air-stable mononuclear orthometalated ruthenium(III) 2-(aryloxo)phenolate complexes of the general composition $[RuX(Asph_3)_2(L)]$ ($X=Cl$ or Br ; $L=CNO$ donor of the 2-(aryloxo)phenolate ligands) have been synthesized and characterized by IR, UV-Vis, and EPR as well as by element analysis.



A group of six ruthenium(III) complexes of type $[\text{Ru}(\text{acac})(\text{L})_2]$ where $\text{acac} = \text{acetylacetonate}$ anion and $\text{L} = 2\text{-(arylazo)-4-methylphenolate}$ anion or $1\text{-phenylazo-2-naphtholate}$ anion have been synthesized and characterized. Structural characterization of a representative complex, where $\text{L} = 1\text{-phenylazo-2-naphtholate}$ anion, shows that the azophenolate ligands are coordinated as N,O -donor ligands forming six-membered chelate rings. The complexes are paramagnetic (low-spin d^5 , $S=1/2$ and show rhombic ESR spectra in 1:1 dichloromethane-toluene solution at 77 K. In carbon tetrachloride solution these complexes show intense LMCT transitions in the visible region together with weak ligand-field transitions in the near IR region. All the complexes display two cyclic voltammetric responses, a ruthenium(III)-ruthenium(IV) oxidation in the range of 0.83 to 1.03V vs SCE and a ruthenium(III)-ruthenium(II) reduction in the range of -0.24 to -0.52V vs SCE. Formal potentials of both the couples correlate linearly with the Hammett constant of the para substituent in the arylazo fragment of the 2-(arylazo)-4-methylphenolate ligand. The ruthenium(IV) and ruthenium(II) congeners of the $[\text{Ru}(\text{acac})(\text{L})_2]$ complexes have been generated by chemical or electrochemical methods and they have been characterized by electronic spectroscopy and cyclic voltammetry.

A series of mononuclear organoruthenium complexes of the type $[\text{RuX}(\text{pph}_3)(\text{L})]$ or $[\text{RuBr}_3(\text{pph}_3)_2(\text{L})]$; $\text{L} = 2\text{-(arylazo)phenolate}$ ligand have been synthesized from the reaction of five 2-(arylazo)phenol ligands with ruthenium(III) precursors, viz. $[\text{RuCl}_3(\text{pph}_3)_3]$ and $[\text{RuBr}_3(\text{pph}_3)_2](\text{CH}_3\text{OH})$ in benzene under reflux. In all these reactions, the 2-(arylazo)phenolate ligand replaces one triphenylphosphine molecule, two chloride or bromide and one methanol from the precursors leading to five-membered cyclometallated



species. The 2- (arylo) phenol ligands behave as dianionic C,N,O donor and coordinated to ruthenium by dissociation of the phenolic proton and the phenyl proton at the ortho position of the ring. The compositions of the complexes have been established by element analysis, magnetic susceptibility measurement, FT-IR, UV-Vis and EPR spectral data. These complexes are paramagnetic and show intense d-d and charge transfer transition in chloroform. The solution EPR spectral of the complexes in dichloromethane at 77K shows rhombic distortion around the ruthenium ion. The structural conformation of the complex 1 has been carried out by X-ray crystallography.

Ruthenium(II) cyclometallated complex containing para-chloroacetophenone thiosemicarbazone (L) of formula $[\text{Ru}(\text{L})(\text{CO})(\text{PPh}_3)_2]$ has been synthesized and characterized by elemental and spectral analyses. The thiosemicarbazone ligand coordinates to ruthenium as a tridentate C, N, and S donor generating two five membered metallacycles. The crystal structure analysis of the complex $[\text{Ru}(\text{L})(\text{CO})(\text{PPh}_3)_2]$ indicates the presence of a distorted octahedral geometry. The complex shows a quasi-reversible one electron oxidation (Ru(III)/Ru(II)) at 0.78 V vs SCE. Further, the catalytic transfer hydrogenation of substituted acetophenones by the titled complex was carried out with conversions up to 99.3% in the presence of *i*-PrOH/KOH.

Reaction of 2-(arylo)phenols with $[\text{Ru}(\text{PPh}_3)_2(\text{CO})_2\text{Cl}_2]$ affords a family of organometallic complexes of ruthenium- (II) of type $[\text{Ru}(\text{PPh}_3)_2(\text{CO})(\text{CNO-R})]$, where the 2-(arylo)phenolate ligand (CNO-R; R = OCH₃, CH₃, H, Cl, and NO₂) is coordinated to the metal center as tridentate C,N,O-donor. Another group of intermediate complexes of type $[\text{Ru}(\text{PPh}_3)_2(\text{CO})(\text{NO-R})(\text{H})]$ has also been isolated, where the 2-(arylo)phenolate ligand (NO-R) is coordinated to the metal center as bidentate N,O-donor. Structures of the $[\text{Ru}(\text{PPh}_3)_2(\text{CO})(\text{NO-OCH}_3)(\text{H})]$ and $[\text{Ru}(\text{PPh}_3)_2(\text{CO})(\text{CNO-OCH}_3)]$ complexes have been determined by X-ray crystallography. All the complexes are diamagnetic and show characteristic ¹H NMR signals and intense MLCT transitions in the visible region. Both the $[\text{Ru}(\text{PPh}_3)_2(\text{CO})(\text{NO-R})(\text{H})]$ and $[\text{Ru}(\text{PPh}_3)_2(\text{CO})(\text{CNO-R})]$ complexes show two oxidative responses on the positive side of SCE.

Experimental Methods

Material And Instrumentation

Commercial RuCl₃.3H₂O was purchased from Himedia. All the reagents used were chemically pure and are of analytical reagent grade. The solvents were purified and dried according to standard procedures. 2-aminobiphenyl and *p*-substituted phenols were purchased from S.D. Fine-Chem Limited, India. The precursor complex $[\text{Ru}(\text{II})(\text{p-Cymene})\text{Cl}_2]$ was prepared by reported literature method [1].

The Infrared spectra FT-IR Spectrum of the complexes were recorded in CARY 360, Agilent resolution pro spectrophotometer. Electronic spectrum of the complexes in chloroform was recorded on a Cary 300 Bio-UV-Vis spectrophotometer.

Preparation of 2-(biphenylazo)Phenol Ligands (HL₁-HL₃)

1.38g (10mmol) of 2-aminobiphenyl in 2ml of concentrated hydrochloric acid is dissolved in 10ml of water of a small beaker diazotized by the addition of a solution of 0.5g of NaNO₂ in 10ml of water. A solution of 10mmol of *p*-substituted phenols (HL₁-HL₃; R=OCH₃, ^tButyl, Cl) in 50ml of 10% sodium hydroxide solution in a 100ml beaker is cooled to 0 to 4°C by immersion in an ice-bath, assisted by the direct addition of about 25g of crushed ice, stirred the phenol solution vigorously and added the cold diazonium salt solution very slowly a red precipitate of 2-(biphenylazo)phenol is separated out. When all the diazonium salt solution has been added, allowed the mixture to stand in an ice bath for 30 minutes



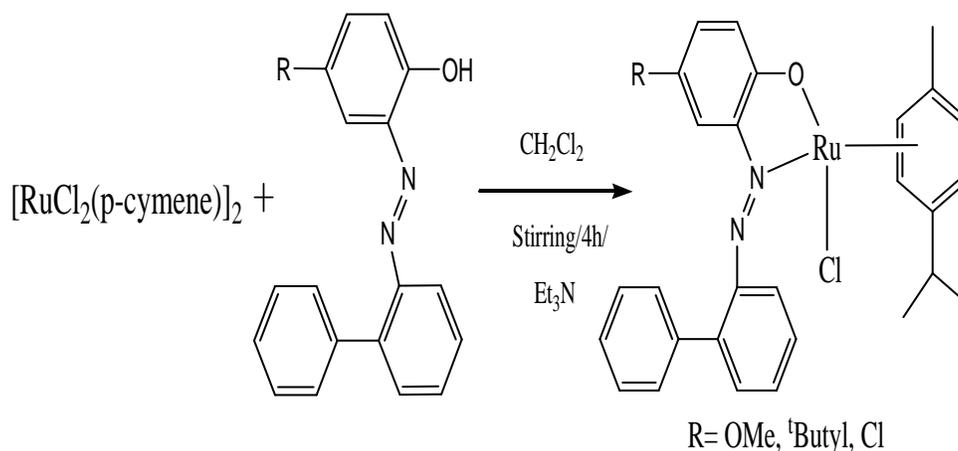
with occasional stirring. Filtered the solution through a buchner funnel with gentle suction, washed well with water and drained thoroughly by pressing the crystals with the back of a large glass stopper. The yield of red colored compounds is about 3g.

Synthesis of Ru(II)(p-cymene) 2-(biphenylazo) Phenolate Complexes [Ru (L₁-L₃)

The ruthenium precursor [RuCl₂(p-cymene)] (0.05g) and 2-(biphenylazo) phenol ligands (HL₁-HL₃) (0.025g) were taken in 1:1 molar ratio in dichloromethane and kept stirring for 4h. Then the solvent was removed through vaccum, the dark red mass was dissolved in chloroform (5 ml) and filtered through short path of silica gel column to remove insoluble materials. The red solution was then concentrated into 2 ml, an addition of excess hexane, dark-red product separated out, washed with diethylether and dried in vaccum.

Results and Discussion

The reaction of 2-(biphenylazo)phenolate ligands with chloro-bridged (p-cymene) ruthenium precursor [RuCl₂(p-cymene)]₂ in methanol at room temperature in 1:1 molar ratio resulted in the formation of conformationally rigid new monomeric ruthenium(II) complexes (Scheme 1). The complexes were found to be air stable and are soluble in polar solvents such as chloroform, dichloromethane and acetone, but insoluble in non-polar solvents such as pentane and hexane.



Scheme.1 Synthesis Of P-Cymene Ru(II) 2-(Biphenylazo)Phenolate Complexes

IR Spectra

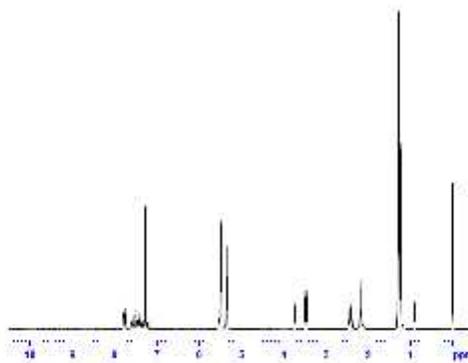
Infrared spectrum of the complexes [Ru(L₁₋₃)(Cl)(p-cymene)] exhibit many sharp and strong vibration within 4000-600cm⁻¹. However, in the free ligand, the bands around 1467-1434cm⁻¹ and 1246-1204cm⁻¹ corresponding to (N=N) and phenolic (C-O) respectively. On complexation, (N=N) appears at lower frequency in the range 1389-1387cm⁻¹ and this red shift supports the coordination of N(azo) to ruthenium ion [1]. The band corresponding to phenolic (C-O) stretching is shifted to higher frequency in the range 1265-1249cm⁻¹ in the complex confirming that the other coordination site is the phenolic oxygen [2]. This was further supported by the disappearance of (OH) band in the range 3430cm⁻¹ in the complexes [1-3].

Electronic Spectra

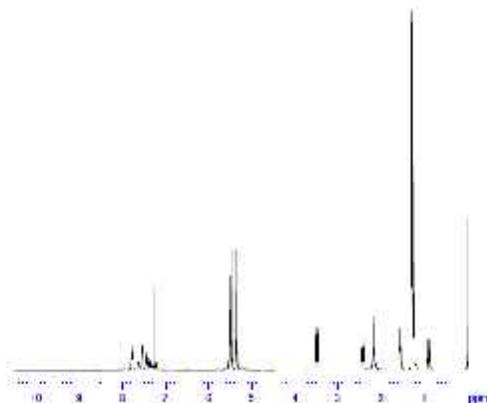
Electronic spectra of the complexes have been recorded in dichloromethane solution in the range 800-200nm. The absorption at 410–418 nm are probably due to metal-to-ligand charge transfer transitions.



The charge transfer transitions taking place from the highest filled ruthenium t^2 orbital (highest occupied molecular orbital) to the vacant π^* (-N=N-) orbital of the 2-(biphenylazo) phenolate ligand (lowest unoccupied molecular orbital) or to the higher energy vacant orbitals of other fragment of ligands. It has been observed that many charge-transfer transitions in such mixed-ligand complexes may result from the lower symmetry splitting of the metal level, the presence of different acceptor orbitals, and the mixing of singlet and triplet configurations in the excited state through spin-orbit coupling. In addition, the other high intensity bands in the 330–252 nm regions were characterized by ligand-centered (LC) transitions taking place in the coordinated 2-(biphenylazo)phenolate ligands.



$^1\text{H-NMR}$ Spectra for p-cymene Ru(II) 2-(biphenylazo)phenolate complex(1)



$^1\text{H-NMR}$ Spectra for p-cymene Ru(II) 2-(biphenylazo)phenolate complex(2)



Conclusion

P-cymene ruthenium(II) 2-(biphenylazo)phenolate complexes have been synthesized by the reaction of $[(RuCl_2(p-cymene))]_2$ with 2-(biphenylazo)phenolate ligands in 1:1 molar ratio in dichloromethane. These new ruthenium(II) complexes have been characterized by analytical and spectral (IR, UV-Vis and 1H -NMR) methods and the octahedral structure is proposed for these complexes.

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